STANNIC OXIDE AND INDIUM OXIDE FILMS AS AIR ELECTRODES FOR HIGH TEMPERATURE COAL REACTING FUEL CELLS

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I. INTRODUCTION

A high temperature fuel cell using a zirconia ceramic electrolyte is being developed because of its potential for generating electric power with high efficiency by reacting conventional hydrocarbon fuels with oxygen from air. Each cell consists of three layers -- an electronically conducting air electrode -- the electrolyte which at 1000°C is a good oxygen ion conductor and the fuel electrode, another good electronic conductor. Oxygen from the air stream picks up electrons from the air electrode to form oxygen ions. These are conducted through the electrolyte to react with the fuel gases delivering electrons to the fuel electrode. Oxidation of the fuel is controlled by the flow of electrons through the external electrical load connected between the two electrodes.

Electronically conducting oxides are being studied as possible air-electrodes for these fuel cells. A class of oxides has been identified which: (1) display high electronic conductivity, (2) are compatible with the ceramic electrolyte, (3) are stable in air atmospheres at the fuel cell operating temperatures -- 1000°C, and (4) are relatively inexpensive. Coatings of these materials have been applied to electrolyte test samples and the voltage losses (polarization) associated with their operation as air electrodes measured. These tests identify indium oxide, In_2O_3, doped with tin, antimony, or tellurium, and tin dioxide, SnO_2, doped with antimony or tellurium as possible electrode materials. Indium oxide appears especially promising in view of the similarity of its crystal structure and thermal expansion properties to those of the electrolyte.

II. ELECTRICAL CONDUCTIVITY IN TIN AND INDIUM OXIDES

In stannic oxide (SnO_2) the two 5s electrons and the two 5p electrons of the tin are bonded with the 2p electrons of the oxygen. An energy gap of between 3.5 and 4.2 electron volts exists between the valence and conduction band associated with this configuration.[1,2] The intrinsic conductivity of stannic oxide is enhanced by the addition of antimony donor atoms. Measurements by Imai[3] on antimony-doped tin-oxide films have shown that at, and above, liquid nitrogen temperatures each antimony atom is ionized. At antimony concentrations above 1×10^{-3} mole percent, Loch's[4] conductivity versus temperature measurements indicate that the number of intrinsic conduction electrons and electrons contributed from lattice defects can be neglected in comparison to those provided by the antimony donors. The effects of even larger antimony donor concentrations on electrical conductivity have been reported by Mochel.[5] His results (Figure 1) indicate that the conductivity increases with increasing antimony content up to 1 weight percent Sb_2O_3 and then decreases with further antimony additions. Resistivities of 7×10^{-4} ohm-cm were obtained at room temperature with optimum antimony concentration.

In indium oxide (In_2O_3), the 5s and 5p valence electrons of two indium atoms are bonded with the 2p electrons of three oxygen atoms. An energy gap of 3.1 to 3.5 electron volts exists between the valence and conduction bands.[6] Weiher observes room temperature resistivities of 0.2-3 ohm-centimeters in relatively pure, single crystal samples. Tin, antimony and tellurium will substitute for indium in the indium oxide crystal lattice. These atoms act as donors, contributing electrons to a conduction band at room temperature. Figure 2 shows how the room temperature resistivity depends on the concentration of donor ions in the starting solutions from which these electrode films were prepared. With optimum doping, resistivities were reduced to less than 7 x 10^{-4} ohm centimeters at room temperature. As in tin oxide, the donor atoms in In_2O_3 are completely ionized at room temperature and the temperature coefficient of resistivity is determined by the predominant electron scattering mechanism.(7) At 1000°C, resistivities of about 10^{-3} ohm-cm were observed with optimum tin doping.

The oxides of indium and tin (In_2O_3 and SnO_2) when appropriately doped display electrical resistivities at fuel cell operating temperatures of the order of 10^{-3} ohm-cm. They can be easily applied in thicknesses up to 10^{-2} cm in the case of indium oxide and 10^{-3} cm in the case of tin oxide. Resistivity/thickness values below one ohm can be achieved with either of these materials. This is low enough to make attractive electrodes.

III. APPLICATION OF TIN OXIDE AND INDIUM OXIDE ELECTRODE FILMS TO ZIRCONIA ELECTROLYTES

These oxide electrode materials are easily applied to zirconia electrolytes by a vapor deposition process. Dilute hydrochloric acid solutions of stannic chloride mixed with appropriate amounts of antimony chloride (or indium trichloride mixed with stannic chloride) are sprayed into a furnace which supplies sufficient heat to vaporize the reactant stream. The vapor stream is then carried into a deposition furnace where, on contacting the heated electrolyte, coatings of tin oxide or indium oxide are deposited. Either an inert gas or air can be used to transport the vapor through the deposition system. Control of the concentrations of the various reactants, of the carrier gas flow rate, and of the heat inputs and temperatures of the various furnaces assures reproducible film characteristics. The following considerations apply to the electrode application process: (1) The vaporization furnace temperature and heat input must be sufficiently high to ensure vaporization of the reactants, it must be kept below a value which will cause the formation of significant quantities of the oxide in the gas stream, i.e., the vapor phase reaction of

$$2\,InCl_3 + 3\,H_2O \rightarrow In_2O_3 + 6\,HCl$$

or

$$SnCl_4 + 2\,H_2O \rightarrow SnO_2 + 4\,HCl$$

must be avoided. For the furnace configuration and reactant concentrations used in our experiments the optimum vaporization temperature for the deposition of tin oxide films was between 325 and 430°C. For the deposition of indium oxide films, vaporization furnace temperatures between 850 and 950°C were used. (2) The deposition furnace temperature must be sufficient to promote the oxidation reactions mentioned above on the substrate but must inhibit appreciable vapor phase reaction. Deposition furnace temperatures of 700-750°C were used in our experiments with SnO_2 and 1000°C in our experiments with In_2O_3. Figure 3 shows the deposition apparatus and Figure 4 the appearance of a typical indium oxide film applied by this process.

IV. STABILITY OF ELECTRODE FILMS IN AIR AT 1000°C

Thermodynamic considerations show that the loss of material from an SnO_2 electrode film in an air atmosphere would most likely occur through gradual decomposition to the gaseous monoxide-SnO.(8) A vapor pressure of 10^{-8} atmosphere of SnO over SnO_2 at 1000°C is indicated. Rough estimates of the rate of material loss through saturation of the fuel cell air supply with SnO indicate that an electrode life of over five years can be anticipated. Tin oxide appears to be a stable air electrode material.

Experimental determinations of the equilibrium pressures existing over indium oxide (In_2O_3) at 1000°C indicate that a decomposition to the gaseous sub-oxide (In_2O) is the most likely cause for loss of this electrode material. With an oxygen partial pressure of 2×10^{-8} atmosphere over the In_2O_3 the In_2O vapor pressure is 4×10^{-8} atmospheres.(9) In the presence of an oxygen partial pressure of 0.2 atmosphere corresponding to one atmosphere of air over the electrode, decomposition to In_2O would be inhibited and a vapor pressure of 10^{-15} atm. of In_2O would be expected. In_2O_3 appears to be even more stable that tin oxide and should be suitable for the air electrode.

These considerations do not give any indication of the possible loss of the doping agent from the oxide film. Since loss of the doping agent would cause increases in the resistivity of the film material, tests have been made in which ρ_e/δ_e was measured as a function of time of electrode operation. In test periods of one month there were no measurable changes with either electrode material.

V. STABILITY OF THE ELECTRODE FILM IN CONTACT WITH ZIRCONIA ELECTROLYTE

A. Stannic Oxide (SnO_2) Films

Stannic oxide crystallizes with the tetragonal structure.(10) The material has a coefficient of thermal expansion of 4.5×10^{-6} cm/cm - °C which is roughly one half that of the electrolyte. Films having thicknesses between 10^{-4} and 10^{-3} cm have been successfully applied to the electrolyte by the thermal decomposition of tin-chloride solutions. These films have adhered well and have withstood repeated thermal cycling between room temperature and 1000°C. Films which exceed 3×10^{-3} cm in thickness develop tensile stresses in electrolytes of 0.1 cm thickness which are sufficient to crack the electrolyte when the samples are cooled to room temperature.

Studies of solid state reactions between SnO_2 and ZrO_2 have been made by Stöcker.(11) He finds a solubility of ZrO_2 in SnO_2 of 19 pp 100 moles between 800 and 1300°C and a solubility of SnO_2 in monoclinic ZrO_2 of 9 pp 100 moles at 800°C. Experiments indicated no observable sintering of one-micron tin-oxide powders to electrolyte discs after heating for four hours at 1400°C. At 1600°C, however, the reaction proceeded rapidly and after 20 minutes of exposure the electrolyte material had become frangible. This observation agrees with Stöcker's conclusions that additions of SnO_2 tend to destabilize cubic zirconia. No evidence of alteration of the electrolyte could be seen on photomicrographs of tin oxide coated electrolyte test specimens after 400 hours of electrode operation at 1000°C. It appears that tin oxide electrodes formed from the chlorides are sufficiently stable in contact with the electrolyte to make useful electrode structures.

B. Indium Oxide Films

Indium oxide crystallizes in Tl_2O_3 structure,(10) a deformed cubic fluorite crystal in which three-fourths of the fluorine positions are occupied by oxygen, the remainder remaining vacant. Wyckoff tabulates the lattice parameter as: a_o = 10.118 Å at 26°C. This matches well with the similar spacing in cubic zirconia: $2a_o = 2 \times 5.10$ Å = 10.20 Å. The linear thermal expansion of In_2O_3 single crystal and polycrystalline samples have been measured by Weiher and Ley(12) over the temperature range 0-700°C. Over this range the linear thermal expansion matches that of cubic zirconia (Figure 5). Adherent oxide layers that withstand thermal cycling between room temperature and 1000°C, with or without electrode operation at the high temperature, have been applied to the electrolyte by vapor deposition. Only when the indium oxide layer exceeded 9×10^{-3} cm in thickness was loosening of the electrode film from the electrolyte substrate noted.

To determine whether the electrolyte and indium oxide would interact when held for long times at elevated temperatures, a series of experiments were made in which yttria-stabilized zirconia electrolyte test wafers were imbeded in one micron indium-oxide powder and heated at various temperatures between 1400°C and 1920°C for 20 minutes in an air atmosphere. Below 1500°C no sintering or other evidence of interaction could be detected. Above 1500°C considerable reaction took place. Liquid formation in the vicinity of 1600°C was observed in these tests.

Sintering for twelve hours at 1400°C without detectable interaction make it appear that In_2O_3 electrode films applied by vapor deposition or similar low temperature processes will be stable in contact with the electrolyte under fuel cell operating conditions.

VI. POLARIZATION BEHAVIOR AND ELECTRODE TO ELECTROLYTE CONTACT RESISTANCE LOSSES OF SnO_2 AND OF In_2O_3 ELECTRODES

Vapor deposited tin and indium oxide electrode films were operated as electrodes carrying out the air electrode reaction:

$$\underset{\text{air}}{O_2} \;\Big|\; \underset{\text{electrode}}{+\,4e} \;\Big|\; \to 2O^{=} \;\Big|\; \text{electrolyte}$$

The voltage losses associated with carrying out this process were measured using the electrode tester and monitoring the electrode to electrolyte voltage as a function of electrode current density. The current-interruption technique[13] was used to separate the ohmic losses associated with oxygen ion transport in the electrolyte and the electrode to electrolyte contact resistance from non-ohmic, "polarization", voltage losses.

The electrical behavior of a typical indium oxide electrode film in its "as deposited" condition is shown in Figure 6. Polarization voltage drops increase very rapidly with electrode current. At 100 ma (77 ma/cm^2) the polarization component of the voltage (50 millivolts) agrees very well with the expected ohmic contribution from the electrolyte ionic resistance -- indicating a negligible electrode-to-electrolyte contact resistance. The character of the decay of the polarization voltage drop, as shown by the current-interruption oscillograms, changes when the polarization voltage exceeds approximately 700 millivolts. The volt-ampere curve becomes almost parallel to the ohmic resistance displaced by the 700 millivolt polarization. The time constant of polarization decay is long and depends upon the length of time the electrode has been operated. A partial electrochemical-reduction of the In_2O_3 electrode is apparently responsible. The long decay of the polarization results from the reoxidation of the partially reduced film when current flow is interrupted.

Apparently, the "as deposited" indium oxide films are sufficiently impervious to the passage of oxygen that high polarization voltage drops occur at even low current densities (oxygen demands). The value of the current, at which electrochemical breakdown of the indium oxide film occurs is inversely proportional to the electrode thickness (Figure 7).

Some treatment must be employed to yield electrodes capable of high current densities with low polarization losses. Fortunately, a simple "reverse current" treatment of the electrode film results in greatly improved performance. Reverse current treatment consists simply of applying a voltage across the electrode-electrolyte interface with the indium oxide made positive with respect to the electrolyte. Under these conditions oxygen is transported through the electrolyte toward the electrolyte-electrode interface. It may be theorized that an oxygen pressure is developed under the electrode film which opens oxygen paths through the previously tight film. When the electrode is operated in the normal direction, polarization voltage losses are greatly reduced. Some increase in the electrode to electrolyte contact resistance may accompany the reverse current treatment.

Figure 8 compares the volt-ampere characteristics of a typical electrode film before and after reverse current treatment. The resistive component of the electrode to electrolyte voltage drop has increased from the calculated value of the electrolyte contribution, 0.48 ohm, to 0.67 ohm while the polarization component has dropped from 730 mv to 150 mv at a current density of 380 ma/cm^2. At a current density of 770 ma/cm^2 the polarization component of the voltage loss is 220 mv.

The polarization characteristics in oxygen of five vapor deposited electrodes after reverse current treatment are shown in Figure 9. The electrodes cover a range of electrode weights from 8 to 37 milligrams per square centimeter of electrolyte coverage. (This corresponds to a range of operating ρ_e/δ_e from 2.6 ohm centimeter per cm to 0.4 ohm cm/cm.) Polarizations are seen to increase from a value between 30-90 mv at 100 ma/cm^2 to between 120-230 mv at 1000 ma/cm^2. A limiting-current type of polarization behavior is displayed suggesting that further efforts to increase the permeability of the electrode film to oxygen may be expected to yield lower polarizations. Tin oxide films performed less satisfactorily. The films tested experimentally displayed electrode resistivity/thickness parameters of three ohms. (Improvements in film application techniques together with optimized doping of the electrode, should make ρ_e/δ_e values less than one ohm attainable.) High values of ρ_e/δ_e in electrode coatings results in a non-uniform current density distribution in the test samples. This complicates the interpretation of polarization losses. The experiments indicated that polarization losses were comparable with those reported for In_2O_3 films (perhaps even somewhat lower due to the tendency of the SnO_2 films to craze under the differential thermal expansion stresses) but that contact resistances between electrode and electrolyte were appreciably higher. It appears that the electrode performance could be significantly improved through the use of better application techniques, optimized doping, and the use of a porous structure.

VII. CONCLUSIONS

Indium sesquioxide, doped with tin, antimony, and/or tellurium, was found to be a promising air electrode for solid electrolyte fuel cells operating at 1000°C. The material is stable in air and in contact with the electrolyte. It can be easily applied in films having a resistivity/thickness parameter as low as 0.2 ohm-cm/cm at the operating temperature. Although polarization voltage losses of the "as deposited" films are high, a simple reverse current treatment reduces polarization losses to 150-250 mv at 1000 ma/cm^2. Increasing the porosity of the In_2O_3 films further reduces the air electrode poalrization. Electrodes of the doped indium oxide have operated for over 1100 hours at a current density of 770 ma/cm^2 with polarization voltage loss of 50 mv, constant electrode resistivity ÷ thickness parameter, and with no measurable contact resistance to the electrolyte (Figure 10).

Tin oxide doped with antimony or tellurium can also be applied to zirconia electrolytes by the thermal decomposition of aqueous solutions of tin and antimony or tellurium chloride. The films are stable at the 1000°C operating temperature of the fuel cell. Despite a lower coefficient of thermal expansion, tin oxide films withstand repeated thermal cycling between room temperature and 1000°C. When operated as electrodes, a weakening of the electrode to electrolyte bond occurs and and the electrode flakes off as it is subsequently cooled through the range 800-600°C. If tin oxide is to be used as an electrode in practical devices, some method must be developed to keep the electrode attached to the electrolyte during cooling.

These materials are suitable as air electrodes. They promise to play an important role in making practical solid electrolyte fuel cell devices.

REFERENCES

1. E. E. Kohnke; J. Phys. Chem. Solids, Vol. 23, pp 1557-1562, 1962.
2. K. Ishiguro, T. Sasaki, T. Arai, & I. Imai; J. Phys. Soc. of Japan 13, pp 296-304, March 1958.
3. I. Imai; J. Phys. Soc. of Japan 15, 937-938, 1960.
4. L. D. Loch; J. Electrochem. Soc. 110 (10), 1081-1083 (1963).
5. J. M. Mochel; U.S. Patent 2,564,706, August 1951.
6. R. L. Weiher; Elec. Properties of Single Crystals of Indium Oxide; J. Appl. Phys. 33,9, '63.
7. E. F. Sverdrup, A. D. Glasser, D. H. Archer, Twenty-Fifth Monthly Progress Report, Office of Coal Research, Contract 14-01-001-303, January 1965.
8. Ibid.
9. R. P. Burns, G. DeMaria, J. Dowart & M. Inghreen; J. Appl. Physics, 38, 1963, pp 1035-36.
10. Wyckoff, R. W. G., Crystal Structures, Interscience, New York, 1951.
11. Stöcker, H. J., A Contribution to the Study of the Properties of Zirconia-Base Refractory Solid Solutions and the Stabilization of Cubic Zirconia, Annales de Chimie, 1960, 1459-1509.
12. Weiher, R. L. and Ley, R. P., J. Appl. Phys., 34, 1963, 1833-34.
13. E. F. Sverdrup, D. H. Archer, J. J. Alles, and A. D. Glasser, Testing Electrodes for High Temperature Solid-Electrolyte Fuel Cells, Hydrocarbon Fuel Cell Technology, Academic Press Inc., New York, 1965, pp 311-333.

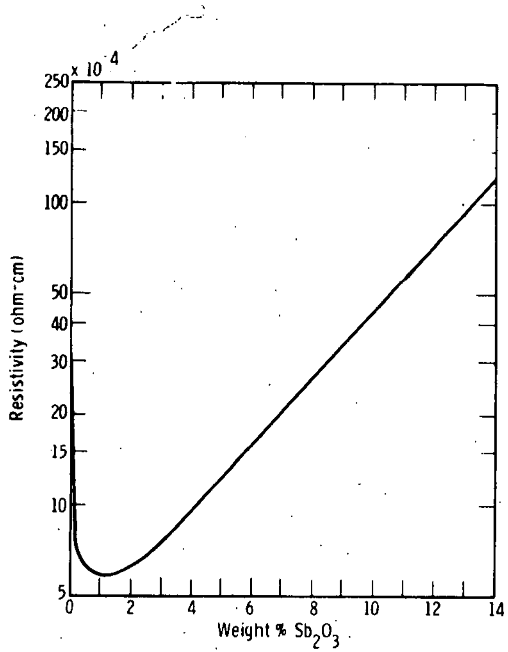

Fig. 1—Effect of antimony doping on the room temperature resistivity of tin oxide (after Mochel, U. S. Patent 2,564,706)

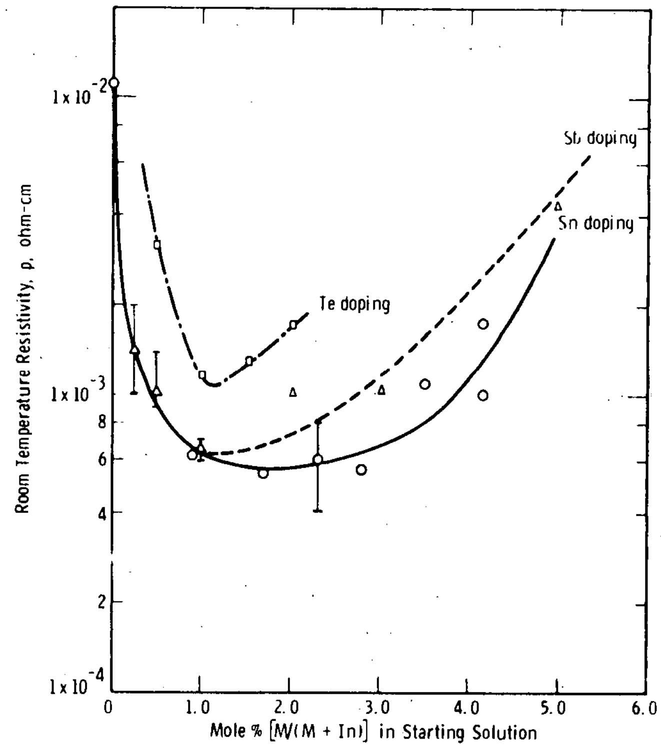

Fig. 2 Effect of doping on the resistivity of Indium Sesquioxide
M = O Sn doping
M = Δ Sb doping
M = □ Te doping

Figure 3 - Vapor Deposition of Indium Oxide Air Electrodes

Figure 4 - Indium Oxide Air Electrode

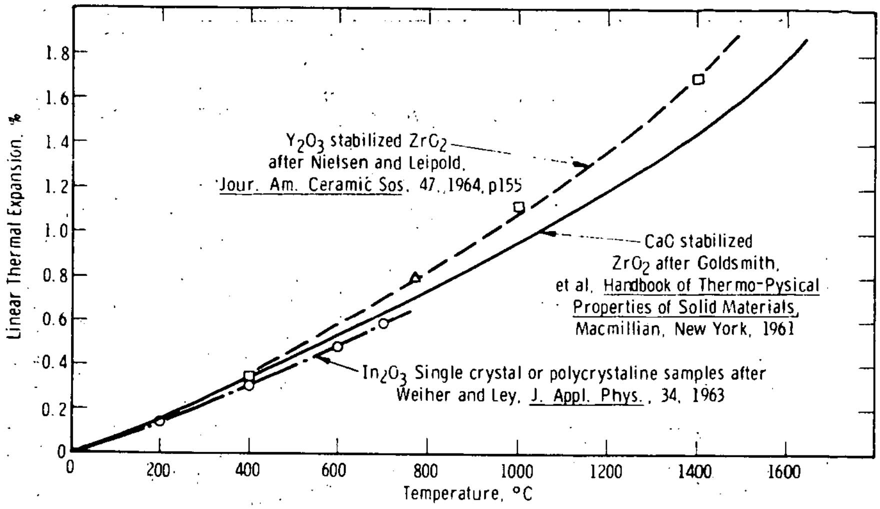

Fig.5—A comparison of the linear thermal expansion characteristics of In_2O_3 and stabilized cubic Zirconia

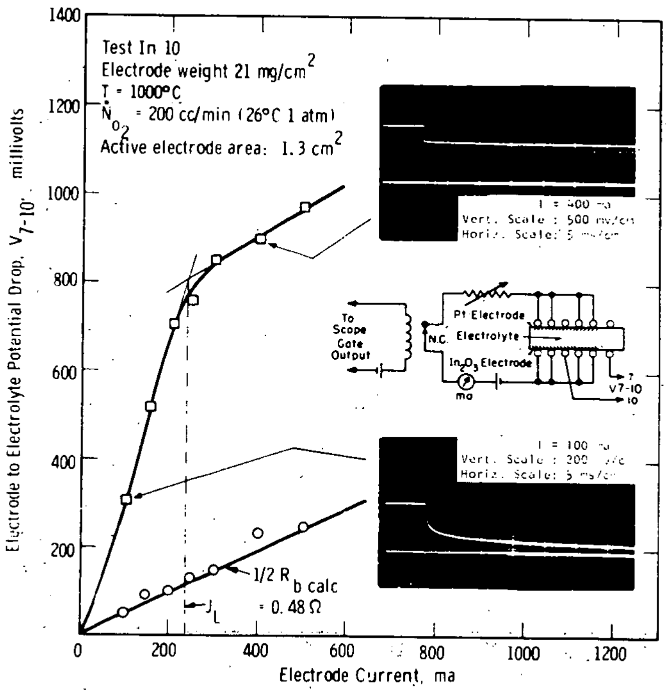

Fig. 6—Volt-ampere characteristic of Indium Sesquioxide air electrode prior to treatment-showing the nature of the polarization

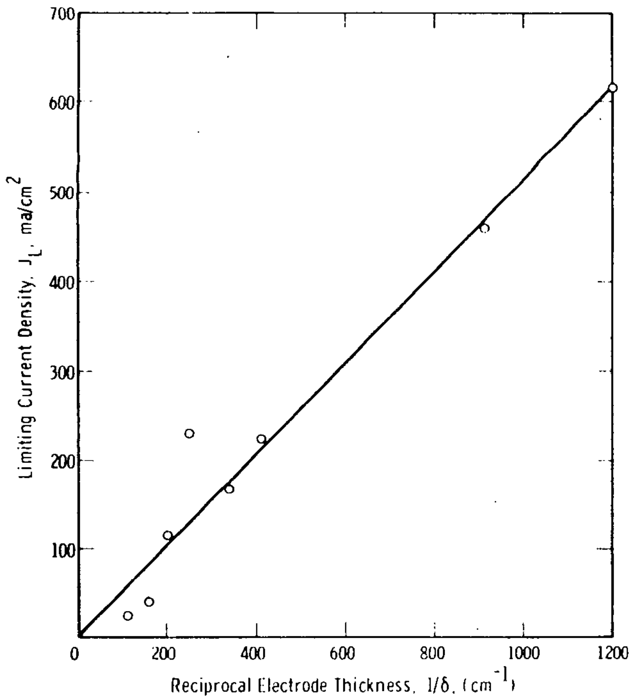

Fig. 7–The effect of electrode thickness on J_L, the current density at which the break in the voltage-current curve appears (see Fig. 8)

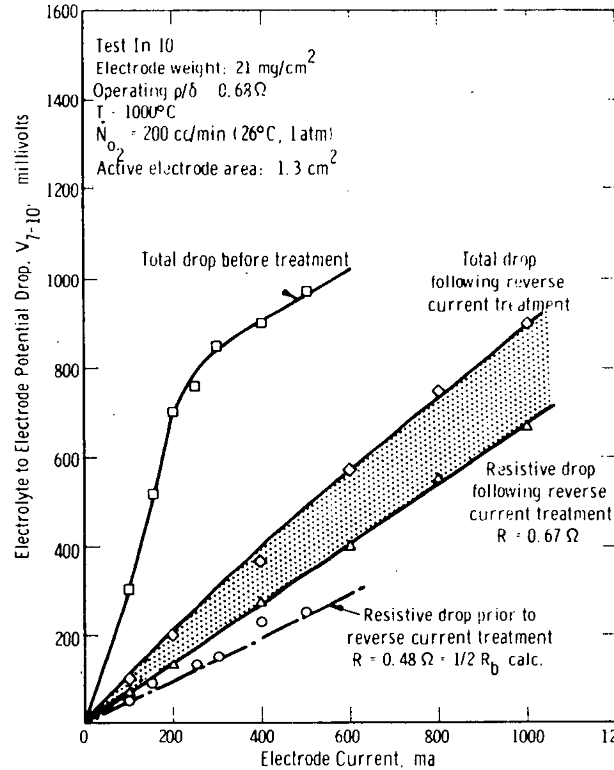

Fig. 8–Volt-ampere characteristic of Indium Sesquioxide air electrodes before and after "reverse current" treatment

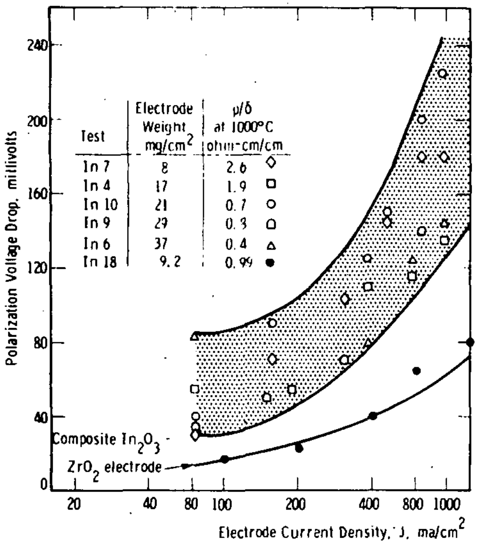

Fig. 9–Indium Sesquioxide electrode polarization following reverse current treatment (1000°C, 1 atm O_2)

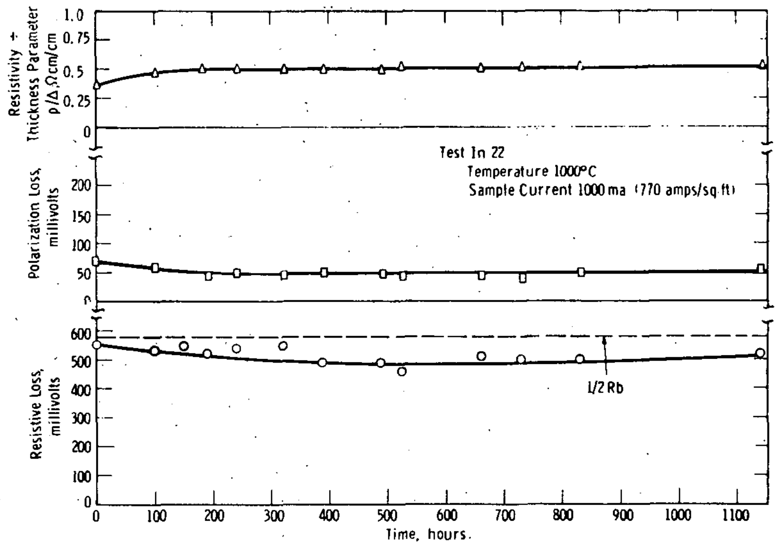

Fig. 10–Life test of a composite In_2O_3 air electrode

(Terminated because of failure of Platinum electrode - loss of In_2O_3 from spots around edges made retesting impossible)